

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP014240

TITLE: Hardness and Abrasion Resistance of Nanocrystalline Nickel Alloys Near the Hall-Petch Breakdown Regime

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings Volume 740 Held in Boston, Massachusetts on December 2-6, 2002. Nanomaterials for Structural Applications

To order the complete compilation report, use: ADA417952

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP014237 thru ADP014305

UNCLASSIFIED

## Hardness and Abrasion Resistance of Nanocrystalline Nickel Alloys Near the Hall-Petch Breakdown Regime

Christopher A. Schuh<sup>1</sup> and T. G. Nieh<sup>2</sup>

<sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology  
77 Massachusetts Avenue, Room 8-211, Cambridge, MA 02139, USA

<sup>2</sup>Materials Science and Technology Division, Lawrence Livermore National Laboratory  
7000 East Avenue, L-350, Livermore, CA 94550, USA

### ABSTRACT

The breakdown of classical Hall-Petch scaling remains an area of scientific interest, and will govern the limiting strength of nanocrystalline alloys for structural applications. In this work we discuss the hardness and scratch resistance of nanocrystalline nickel and nickel-tungsten solid solution alloys, assessed through nanoindentation and nano-scratch techniques. The materials have been prepared by electrodeposition, and are fully dense with grain sizes between 6 and 22 nm. In this range of grain sizes, there is some evidence for a breakdown of Hall-Petch scaling, reflected in both the hardness and abrasion data. The role of solid solution alloying on this breakdown is also discussed.

### INTRODUCTION

The grain size of metals can now be varied through a broad range, including the sub-microcrystalline and nanocrystalline regimes, owing to the development of novel processing methods. For example, severe plastic deformation techniques [1, 2] are applicable to most alloys, and can produce grain sizes below one micron. Compaction of nano-powders or nanocrystalline powders offers the possibility of finer grain sizes below 100 nm [3, 4], as do several deposition-based methods such as electrodeposition [5, 6]. The development of nanocrystalline alloys has been driven technologically, by the promise of exceptional properties, as well as scientifically, by the potential breakdown of classical scaling laws and the accompanying need for new materials physics in the nanostructured limit. For example, Hall-Petch strengthening (strength increasing as the inverse square-root of grain size) is expected to break down for grain sizes in the range of 5-30 nm [7] and in fact should give way to a weakening trend toward the amorphous limit. Such an inflection is not only scientifically interesting, but also sets the physical limit for strengthening of nanostructured engineering materials.

Hall-Petch scaling and its possible breakdown in the nanocrystalline regime have been investigated experimentally and theoretically by many authors. The purpose of the present work is to extend the discussion of Hall-Petch breakdown to consider, firstly, the possible roles that solid-solution alloying may play with regard to this effect, and secondly, the implications of Hall-Petch breakdown for abrasion resistance in nanostructured materials. These issues have particular relevance with regard to next-generation micro electromechanical systems made by electrodeposition-based "LIGA" processes.

## EXPERIMENTAL PROCEDURES

Foils of nanocrystalline nickel (n-Ni) and nickel-tungsten (n-Ni-W) were fabricated by direct current (DC) electrodeposition, using standard procedures given in more detail in Refs. [8, 9]. In the case of n-Ni, a nanocrystalline structure is induced through the inclusion of a small amount (5 g/L) of saccharine in the plating bath, and for both n-Ni and n-Ni-W alloys the grain size, morphology, and texture of the plated foils can be tailored to some degree through the choice of bath pH and applied current density [8, 9]. The as-deposited foils were characterized by X-ray diffraction, and their grain size determined by applying the Scherrer formula for peak broadening to the (200), (220), or (111) reflections after correction for instrumental line broadening using a silicon standard. Some specimens were also examined by transmission electron microscopy (TEM) in a Philips CM300 or a JEM-4000EX.

Indentation testing was performed in an MTS/Nanoindenters (Oak Ridge, TN) Nanoindenter-XP, as well as a TriboIndenter instrumented nanoindenter (from Hysitron, Minneapolis, MN), in all cases with a diamond Berkovich indenter. Hardness was determined both by the Oliver-Pharr method and the continuous stiffness method [10], with the instantaneous contact area determined using the calibrated area function of the Berkovich tip. Indentations were performed both on the planar surface and polished cross-sections of the electrodeposited foils; the reported results are average values of more than ten indents.

Abrasive nano-scratch experiments were performed on n-Ni using the Nanoindenter-XP over a travel distance of 500  $\mu\text{m}$ , with a ramping normal load from 20 to  $1.5 \cdot 10^5 \mu\text{N}$ . The diamond tip was oriented such that an edge of the Berkovich pyramid was pointing in the direction of travel. At least three identical scratches were performed on each material; the scratch profiles were always very consistent.

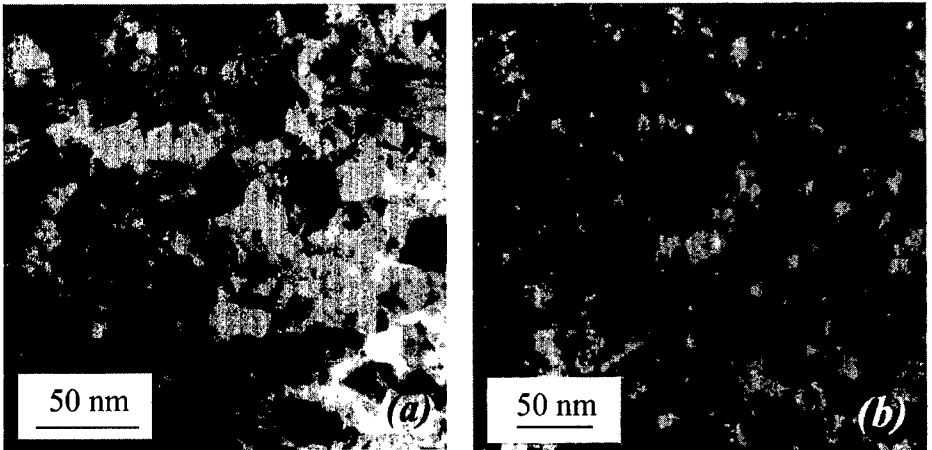


Figure 1: Bright-field TEM images of (a) n-Ni and (b) a n-Ni-W alloy, with nominal grain sizes  $d = 14$  and  $7$  nm, respectively.

## RESULTS AND DISCUSSION

### Materials

For nominally pure n-Ni, specimens with grain sizes in the range 12-22 nm were produced by electrodeposition, while for alloyed n-Ni-W alloys the grain size was somewhat smaller, in the range 6-10 nm, as revealed by the x-ray line broadening measurements. 12 and 6 nm are the smallest grain sizes we were able to produce in Ni and Ni-W, respectively; further attempt to reduce the grain size by adding nucleant in the electrodeposition bath was found impossible without producing some amorphous phases. TEM observations of the grain structure were found to give similar values to the x-ray measurements (within  $\pm 2$  nm), and additionally verified that the specimens were free of porosity. Typical nanostructures observed in the foil normal direction are illustrated in Fig. 1 for both a pure Ni (a) and a Ni-W alloy (b). Chemical analysis revealed that all of the Ni-W alloys had a similar global composition, Ni-(11.6-14.1 at%)W. Additional details about these materials, their processing and structure are available in Refs. [8, 9].

### Hardness and Deviations from Hall-Petch Behavior

The results of the instrumented indentation experiments are summarized as a function of grain size in the Hall-Petch plot of Fig. 2. For comparison, this plot also contains hardness data on nominally pure nickel from the work of Erb et al. [11, 12], who used pulsed-current electrodeposition to produce materials, as well as Ebrahimi et al. [13], who prepared specimens by DC electrodeposition. To a grain size as fine as  $d = 14$  nm and hardness as high as  $\sim 6.4$  GPa, the present data for n-Ni are in reasonable agreement with the classical Hall-Petch scaling behavior, and complement the data of Ebrahimi et al. [13]. However, between the smallest grain sizes of  $d = 14$  and 12 nm, our data show a significant decrease in hardness, consistent with Hall-Petch breakdown anticipated at these grain sizes [7].

The peak hardness of  $\sim 6.4$  GPa observed for n-Ni at  $d = 14$  nm is in agreement with the peak hardness measured by Erb et al. [11, 12] near the same grain size (see Fig. 2), as is the observation of a Hall-Petch breakdown. However, our data reflect a rather abrupt breakdown point near  $d \approx 14$  nm, while the data of Erb et al. [11, 12] show a much broader transition region, spanning grain sizes from 11-25 nm. A possible explanation for this discrepancy lies in the method of sample fabrication. Although both investigations employed electrodeposition techniques to prepare fully dense n-Ni specimens, the present study used direct current plating whereas Erb et al. [11, 12] used pulsed current plating, in which the current is applied as a rectangular wave-form. These methods produce grain structures with different morphologies; our DC electrodeposited foils have an elongated grain structure in the plating direction, as described in Ref. [8]. Additionally, pulsed-current plating gives a rather broad grain size distribution that would tend to broaden the observed Hall-Petch breakdown in Fig. 1 [11, 12].

As described above, both our data and those of Erb et al. [11, 12] suggest that the Hall-Petch inflection occurs near  $\sim 12$ -15 nm for pure nickel. In contrast, the data for Ni-W shown in Fig. 1 appear to also exhibit an inflection, but at a finer grain size,  $d \sim 7$ -9 nm; alloying with W apparently causes a decrease in the inflection grain size. Such a decrease is only possible if the addition of W suppresses the deformation mechanism at the finest grain sizes below the

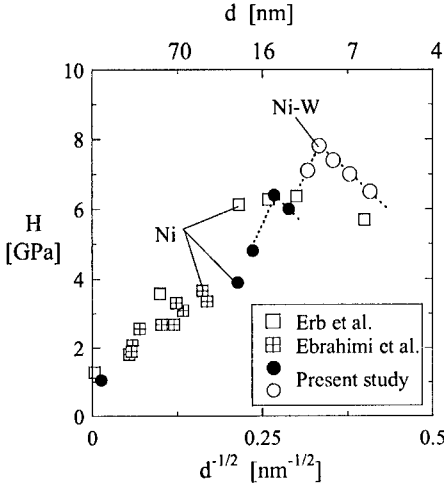


Figure 2: Hall-Petch plot of hardness ( $H$ ) vs. reciprocal square-root grain size ( $d^{-1/2}$ ) for n-Ni and n-Ni-W alloys, compared with data from Refs. [17-19]

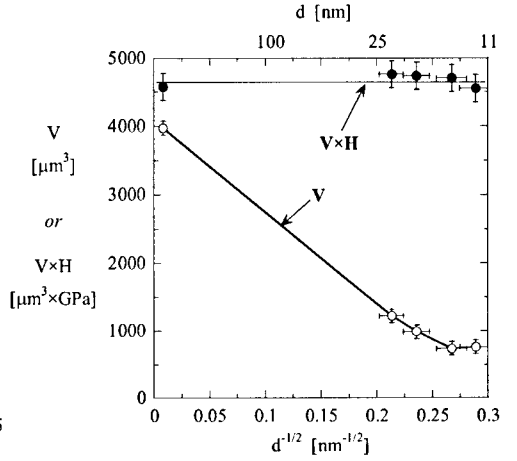


Figure 3: Hall-Petch-style plot of abraded volume ( $V$ ) vs. reciprocal square-root grain size ( $d^{-1/2}$ ) for n-Ni after identical 500  $\mu\text{m}$  scratches with a Berkovich diamond tip.

inflection. Although the detailed deformation mechanisms associated with Hall-Petch breakdown are still under debate, there is general support for diffusional mechanisms such as grain boundary sliding or Coble creep [14, 15]. For such diffusive mechanisms to occur in solid solution alloys such as Ni-W, all of the atomic species of the alloy must redistribute diffusively in order to maintain chemical homogeneity. In a binary alloy deforming in steady state, the deformation is governed by an effective diffusivity, which is a composite of the majority and minority component diffusivities. Assuming a steady-state Coble-creep mechanism to occur below the inflection grain size, and further assuming that the inflection occurs abruptly at a single grain size, it is possible to make an estimate of the inflection grain size for a given concentration,  $c$ , of substitutional element [9]:

$$\frac{d_{\text{Ni-W}}^i}{d_{\text{Ni}}^i} \approx \left[ \frac{D_{\text{W}}}{D_{\text{Ni}}} \cdot (1-c) + c \right]^{2/7} \quad (1)$$

where  $D_{\text{W}}$  and  $D_{\text{Ni}}$  are the grain boundary diffusivities of Ni and W in  $\alpha$ -Ni, and the inflection grain size of the alloy,  $d_{\text{Ni-W}}^i$  is predicted relative to the inflection grain size for pure nickel,  $d_{\text{Ni}}^i$ .

Although there are apparently no quantitative values for the grain boundary diffusion of tungsten in nickel, the volume diffusivity of W in Ni is very much smaller than the self-diffusivity of Ni ( $D_{\text{W}} / D_{\text{Ni}} \approx 5 \cdot 10^{-5}$  at room temperature) [16]. For such a slow diffusing solid solution element it is reasonable to write:

$$\frac{d_{Ni-W}^i}{d_{Ni}^i} \approx c^{2/7} \quad (2)$$

Using an average value for the atomic W concentration in the present alloys,  $c = 0.13$ , this rough calculation gives  $d_{Ni-W}^i / d_{Ni}^i \approx 0.56$ , suggesting that the inflection grain size would be reduced by about a factor of two by alloying Ni with 13% W. If the data for Ni-W in Fig. 2 are interpreted as a Hall-Petch breakdown, then the experimental value for this ratio is in the range  $d_{Ni-W}^i / d_{Ni}^i = 0.47-0.60$ , in excellent agreement with the estimate of Eq. (2). In the case where the diffusional process occurs primarily in the bulk of the nanocrystalline grains (a Nabarro-Herring creep process), the exponent in Eqs. (1,2) would become  $2/5$ . The expected shift in the inflection grain size would then be  $d_{Ni-W}^i / d_{Ni}^i \approx 0.44$ , still in reasonable agreement with the experimental range of  $d_{Ni-W}^i / d_{Ni}^i = 0.47-0.60$ . Thus, the quantitative predictions of Eq. (2) are relatively insensitive to the exact value of the grain size exponent; the general expectation of an inflection grain size smaller by about half is therefore qualitatively reasonable. The very good agreement between model and data may be largely fortuitous, given the many simplifying assumptions of the model and the paucity of experimental data.

The above concepts are not specific to the Ni-W system, but should be generally applicable to most all substitutional solid solutions. Such alloying is theoretically expected to shift the inflection grain size of the Hall-Petch breakdown to smaller values, provided that the alloying element is a slow diffuser, and a diffusive mechanism is in fact responsible for the Hall-Petch breakdown.

### **Nano-Abrasion near the Hall-Petch Breakdown**

Fig. 3 shows a summary of the major results from the nano-scratch experiments on n-Ni, the total volume of displaced material,  $V$ , as determined from atomic force microscope images of the scratches, plotted against  $d^{-1/2}$  in Hall-Petch style. The trend shown in this figure is similar to that observed in hardness (Fig. 2), with a generally linear relationship between  $V$  and  $d^{-1/2}$  from 15  $\mu\text{m}$  down to  $\sim 14$  nm grain sizes. The Hall-Petch hardness breakdown observed below  $\sim 14$  nm in Fig. 2 is manifested here as a deviation from this linear relationship for the specimen with  $d = 12$  nm.

For a rigid asperity scratching a substrate, the amount of material  $dV$  displaced by abrasion is proportional to the distance of translation  $dx$ , and scaled by the projected area of the asperity in the direction of travel. For our experiments, the projected contact area is determined from the ideal geometry of a Berkovich tip, and the applied load increases as a linear function of position, with a proportionality constant  $\kappa = 300$  N/m. Under these conditions one can derive [8]:

$$\frac{dV}{dx} = 0.146 \cdot \frac{\kappa}{H} \cdot x \quad (3)$$

This inverse relationship between hardness and abraded volume can be quantitatively validated by normalizing the wear data in Fig. 3 with the experimental hardness values (from Fig. 2). The solid points in Fig. 3 show the same data, now multiplied by the hardness according to Eq. (3). Whereas the volume of removed material varied by over a factor of five (open points in Fig. 2), normalization with the hardness completely removes this variation to within experimental error.

Thus, although the nanocrystalline nickel specimens used in this work exhibited a broad range of wear resistance, we find that these differences are quantitatively commensurate with the measured change in hardness, even in the limit of the finest grain sizes. Although the breakdown of Hall-Petch strengthening at these grain sizes may be related to a transition in the plastic deformation mechanism, the abrasive wear mechanism appears unchanged through this transition. It is important to emphasize, however, that we have observed an apparent breakdown of Hall-Petch strengthening in pure n-Ni only at a single grain size in this work.

## CONCLUSIONS

The Hall-Petch strengthening of nominally pure Ni is found to hold well into the nanocrystalline regime, with the first suggestion of a breakdown near  $d \sim 14$  nm. This value is in agreement with prior data from the literature, and is significantly different than found in Ni-W alloys, which exhibit an apparent Hall-Petch breakdown near  $d \sim 7$ -8 nm. If diffusional creep mechanisms operate at the finest grain sizes, we find that this result is indeed expected, provided that the solid solution alloying element is a slow diffuser. The Hall-Petch breakdown in n-Ni is also found to manifest itself in the abrasive scratch resistance, which is inversely proportional to hardness.

## ACKNOWLEDGEMENTS

Portions of this work were performed under the auspices of the US Department of Energy by the University of California, Lawrence Livermore National Laboratory, under contract W-7405-Eng-48.

## REFERENCES

- [1] F. H. Froes, O. N. Senkov and E. G. Baburaj, *Mater. Sci. Eng.* **A301**, 44 (2001).
- [2] R. Z. Valiev, I. V. Alexandrov, Y. T. Zhu and T. C. Lowe, *J. Mater. Res.* **17**, 5 (2002).
- [3] G. W. Nieman, J. R. Weertman and R. W. Siegel, *Scripta Metall. Mater.* **24**, 145 (1990).
- [4] P. G. Sanders, J. A. Eastman and J. R. Weertman, *Acta Mater.* **45**, 4019 (1997).
- [5] H. Natter and R. Hempelmann, *Journal of Physical Chemistry* **100**, 19525 (1996).
- [6] L. Lu, M. L. Sui and K. Lu, *Acta Mater.* **49**, 4127 (2001).
- [7] T. G. Nieh and J. Wadsworth, *Scripta Metall. Mater.* **25**, 955 (1991).
- [8] C. A. Schuh, T. G. Nieh and T. Yamasaki, *Scripta Mater.* **46**, 735 (2002).
- [9] C. A. Schuh, T. G. Nieh and H. Iwasaki, *Acta Mater.* (2002), in press.
- [10] W. C. Oliver and G. M. Pharr, *J. Mater. Res.* **7**, 1564 (1992).
- [11] U. Erb, *Nanostructured Materials* **6**, 533 (1995).
- [12] A. M. El-Sharik, U. Erb, G. Palumbo and K. T. Aust, *Scripta Metall. Mater.* **27**, 1185 (1992).
- [13] F. Ebrahimi, G. R. Bourne, M. S. Kelly and T. E. Matthews, *Nanostructured Materials* **11**, 343 (1999).
- [14] V. Yamakov, D. Wolf, S. R. Phillpot and H. Gleiter, *Acta Mater.* **50**, 61 (2002).
- [15] H. Van Swygenhoven, M. Spaczer, A. Caro and D. Farkas, *Phys. Rev.* **B60**, 22 (1999).
- [16] E. A. Brandes and G. B. Brook, eds. *Smithells Metals Reference Book, Seventh Edition*. 1992, Butterworth-Heinemann: Oxford, UK.